

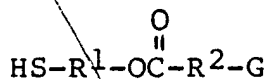
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WHAT IS CLAIMED IS:

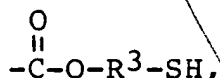
1. In a method for stabilizing a vinyl halide polymer against heat ^{and light} which comprises incorporating a metal-containing stabilizer therein, the improvement which comprises replacing part of the metal-containing stabilizer with an optionally substituted mercaptohydrocarbylene carboxylate.

2. A method according to Claim 1 in which the mercaptohydrocarbylene carboxylate comprises the reaction product of an optionally substituted mercaptohydrocarbylene-ol with a carboxylic acid.

3. A method according to Claim 1 in which the mercaptohydrocarbylene carboxylate has the formula



where R^1 and R^2 , each independently, is optionally substituted hydrocarbylene and G is hydrogen, carboxy or



where R^3 is optionally substituted hydrocarbylene.

4. A method according to Claim 3 in which R^1 and R^3 , each independently, is alkylene of 2 to 20 carbon atoms, R^2 is alkylene of 1 to 20 carbon atoms and R^1 , R^2 and R^3 each independently is alkenylene of 2 to 20 carbon atoms, cycloalkylene of 3 to 8 carbon atoms, arylene of 6 to 20 carbon atoms, alkarylene of 7 to 40 carbon atoms or aralkylene of 7 to 40 carbon atoms; R^1 , R^2 and R^3 being unsubstituted or substituted by one or more of hydroxy, alkoxy of 1 to 20 carbon atoms, oxo, oxirane, alkoxy-carbonyl of 2 to 20 carbon atoms, aryloxycarbonyl of 7 to 20 carbon atoms, acyl of 2 to 20 carbon atoms, acyloxy of 2 to 20 carbon atoms, chloro, bromo, iodo, fluoro, cyano, alkylamido of 2 to 20 carbon atoms, mercapto, alkylthio of 1 to 20 carbon atoms, alkyl-sulfamyl of 1 to 20 carbon atoms, alkylsulfonyl

of 1 to 20 carbon atoms, alkyl of 1 to 20 carbon atoms, aryl of 6 to 20 carbon atoms, alkenyl of 2 to 20 carbon atoms and cycloalkyl of 3 to 8 carbon atoms, and where R^1 , R^2 and R^3 and their substituents are optionally substituted in the chain by one or more of oxygen, sulfur and nitrogen.

B 5. A method according to Claim 4 in which G is hydrogen.

6. A method according to Claim 5 in which R^2 is substituted or unsubstituted alkyl of 1 to 20 carbon atoms or alkenyl of 2 to 20 carbon atoms.

7. A method according to Claim 6 in which R^2 contains 12 to 20 carbon atoms and R^1 is substituted or unsubstituted alkylene of 2 to 20 carbon atoms.

8. A method according to Claim 7 in which R^1 is lower alkylene or hydroxyloweralkylene and R^2 is stearyl, oleyl, linoleyl, myristyl or palmityl.

B 9. A method according to Claim 8 in which the mercapto ester comprises 2-mercaptoethyl stearate, 2-mercaptoethyl oleate, or 2-mercaptoethyl linoleate.

10. A method according to Claim 1 in which the mercaptohydrocarbylene carboxylate comprises an ester obtained by reacting a substituted or unsubstituted mercaptoloweralkanol with a carboxylic acid of 8 to 20 carbon atoms.

B 11. A method according to Claim 1 in which G is

$$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{O}-\text{R}^3-\text{SH} \end{array}$$

12. A method according to Claim 11 in which R^2 is a covalent bond or is substituted or unsubstituted alkylene of 1 to 20 carbon atoms, alkenylene of 2 to 20 carbon atoms, arylene of 6 to 20 carbon atoms, cycloalkylene or cycloalkenylene of 3 to 20 carbon atoms.

13. A method according to Claim 12 in which R¹ and R³, each independently, is unsubstituted or substituted alkylene of 2 to 20 carbon atoms.

14. A method according to Claim 13 in which R² is alkylene of 1 to 20 carbon atoms or alkenylene of 2 to 20 carbon atoms.

15. A method according to Claim 14 in which R¹ and R³ is each lower alkylene or hydroxylower-alkylene.

16. A method according to Claim 4 in which the metal is calcium, barium, zinc, lead, tin or tri-valent antimony.

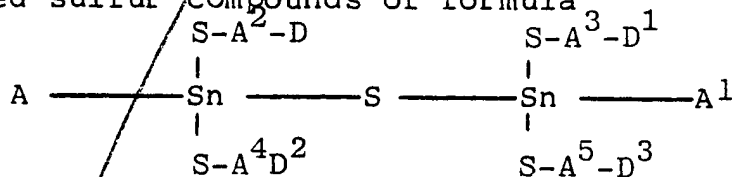
17. A method according to Claim 16 in which the metal is tin.

18. A method according to Claim 17 in which the tin-containing stabilizer comprises a mono- or diorganotin oxide, sulfide, carboxylate, mercaptide, derivative of a mercaptoacid, derivative of a mercaptoalcohol or their esters.

19. A method according to Claim 17 in which the tin-containing stabilizer comprises a compound selected from

dibutyltin maleate
dibutyltin di(stearyl maleate)
[monobutyltin(isooctylmercaptoacetate)-sulfide]
monobutyltin(dodecylmercaptide)sulfide
monobutyltin(mercaptoethyloleate)sulfide
monobutyltin trimercaptoethyloleate
monobutyltin(hydroxyethylmercaptide)(sulfide)

and bridged sulfur compounds of formula



where

A and A¹ are lower alkyl of 1 to 12 carbon atoms;

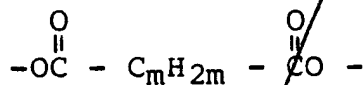
A², A³, A⁴ and A⁵ are lower alkylene

D, D¹, D² and D³ each independently, is

$$\text{OH}, -\overset{\text{O}}{\parallel}\text{OC} - (\text{C}_8 - \text{C}_{20} \text{ alkyl}),$$

$$-(\text{C}_6 - \text{C}_{18}) \text{ alkyl}, \text{ or where}$$

D and D¹, or D² and D³ together form the group



where m is a number from 0 to 8.

tin 20. A method according to Claim 1 in which the ~~metal~~-containing stabilizer is present in an amount to provide up to about 0.25 parts of ~~metal~~ *tin* per 100 parts of polymer and the mercapto ester is present in an amount up to about 6.5 parts per 100 parts of polymer.

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21. In a method for stabilizing a vinyl halide polymer against heat *and light* which comprises incorporating a tin-containing stabilizer therein, the improvement which comprises replacing part of the ~~tin~~-containing stabilizer with a substituted or unsubstituted mercaptoloweralkanol ester of a carboxylic acid containing from 8 to 20 carbon atoms.

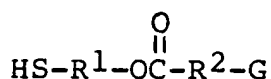
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22. A vinyl halide composition which has been stabilized with respect to heat *and light* by incorporating therein

- a) a metal-containing heat stabilizer in which any oxygen present is bonded to one or more of said metal, carbon, phosphorous and hydrogen, said metal-containing stabilizer being introduced in an amount sufficient to provide up to about 0.25 parts of metal per 100 parts of polymer, and

- b) a mercapto ester comprising the reaction product of an optionally substituted mercaptohydrocarbylene-ol with a carboxylic acid, the mercapto ester being introduced in an amount up to about 6.5 parts per 100 parts of polymer.

23. A composition according to Claim 22 in which the metal of the metal-containing heat stabilizer is calcium, barium, zinc, lead, tin or trivalent antimony and the mercapto ester has the formula



where R^1 and R^2 , each independently, is optionally substituted hydrocarbylene and G is hydrogen, carboxy

or $-\overset{\text{O}}{\parallel}\text{C}-\text{O}-\text{R}^3-\text{SH}$, where R^3 is optionally substituted hydrocarbylene.

24. A composition according to Claim 23 in which R^1 and R^3 , each independently is alkylene of 2 to 20 carbon atoms and R^2 is alkylene of 1 to 20 carbon atoms and R^1 , R^2 and R^3 each independently is alkenylene of 2 to 20 carbon atoms, cycloalkylene of 3 to 8 carbon atoms, arylene of 6 to 20 carbon atoms, alkarylene of 7 to 40 carbon atoms or aralkylene of 7 to 40 carbon atoms; R^1 , R^2 and R^3 being unsubstituted or substituted by one or more of hydroxyl, alkoxy of 1 to 20 carbon atoms, oxo, oxirane, alkoxy-carbonyl of 2 to 20 carbon atoms, aryloxy-carbonyl of 7 to 20 carbon atoms, acyl of 2 to 20 carbon atoms, acyloxy of 2 to 20 carbon atoms, chloro, bromo, iodo, fluoro, cyano, alkylamido of 2 to 20 carbon atoms, mercapto, alkythio of 1 to 20 carbon atoms, alkyl-sulfamyl of 1 to 20 carbon atoms, alkylsulfonyl of 1 to 20 carbon atoms, alkyl of 1 to 20 carbon atoms, aryl of 6 to 20 carbon atoms, alkenyl of 2 to 20 carbon atoms,

and cycloalkyl of 3 to 8 carbon atoms, and where R^1 , R^2 and R^3 and their substituents are optionally substituted in the chain by one or more of oxygen, sulfur and nitrogen.

3 25. A composition according to Claim ~~24~~²² in which G is hydrogen.

26. A composition according to Claim 25 in which R^2 is substituted or unsubstituted alkyl of 1 to 20 carbon atoms or alkenyl of 2 to 20 carbon atoms.

27. A composition according to Claim 26 in which R^2 contains 12 to 20 carbon atoms and R^1 is alkylene of 2 to 20 carbon atoms.

28. A composition according to Claim 27 in which R^1 is lower alkyl or hydroxyloweralkyl and R^2 is stearyl, oleyl, linoleyl, myristyl or palmityl.

29. A composition according to Claim 28 in which the mercapto ester comprises 2-mercaptoethyl stearate or 2-mercaptoethyl oleate or 2-mercaptoethyl linoleate.

30. A composition according to Claim 22 in which the mercapto ester comprises an ester obtained by reacting a substituted or unsubstituted mercapto-loweralkanol with a carboxylic acid of 8 to 20 carbon atoms.

B 31. A composition according to Claim ~~24~~²² in which G is $\begin{array}{c} \text{O} \\ || \\ -\text{C}-\text{O}-\text{R}^3-\text{SH} \end{array}$.

32. A composition according to Claim 31 in which R^2 is substituted or unsubstituted alkylene of 1 to 20 carbon atoms, alkenylene of 2 to 20 carbon atoms or arylene of 6 to 20 carbon atoms.

33. A composition according to Claim 32 in which R^1 and R^3 each independently is unsubstituted or substituted alkylene of 2 to 20 carbon atoms.

B 34. A composition according to Claim 33 in which R^2 is alkylene of 1 to 20 carbon atoms or alkenylene of 2 to 20 carbon atoms. *of 2 to 20 carbon atoms*

35. A composition according to Claim 34 in which R^1 and R^3 is each lower alkylene or hydroxylower-alkylene.

36. A composition according to Claim 24 in which the metal is calcium, barium, zinc, tin or trivalent antimony.

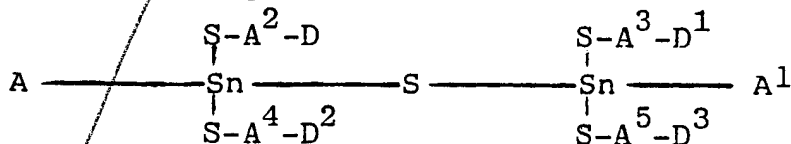
37. A composition according to Claim 36 in which the metal is tin.

38. A composition according to Claim 22 in which the ^{tin}metal-containing stabilizer comprises a mono- or diorgano tin oxide, sulfide, carboxylate, mercaptide, derivative of a mercaptoacid ester or derivative of a mercaptoalcohol or their esters.

39. A composition according to Claim 38 in which the tin-containing stabilizer comprises

dibutyltin maleate
 dibutyltin di(stearyl maleate)
 [monobutyltin(isooctylmercaptoacetate)-sulfide]
 monobutyltin(dodecylmercaptide)sulfide
 monobutyltin(mercaptoethyloleate)sulfide
 monobutyltin trimercaptoethyloleate
 monobutyltin (hydroxyethylmercaptide)(sulfide)

and bridged sulfur compounds of formula



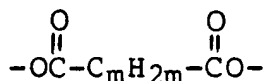
where

A and A^1 are lower alkyl of 1 to 12 carbon atoms;

A^2 , A^3 , A^4 and A^5 are lower alkylene;

D, D¹, D² and D³ each independently,
is

OH, $-\overset{\text{O}}{\parallel}\text{C}-$ (C₈-C₂₀ alkyl),
 $-(\text{C}_6-\text{C}_{18})\text{alkyl}$, or where
 D and D¹, or D² and D³ together form
 the group



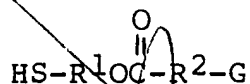
where m is a number from 0 to 8.

40. A composition according to Claim 39 in which
 the mercapto ester is a mercaptoloweralkanol ester of a
 carboxylic acid of 8 to 20 carbon atoms.

41. A composition comprising

- a) a metal-containing heat stabilizer for
 vinyl halide polymers in which any oxygen
 atoms present are bonded to one or more
 of said metal, carbon, phosphorus and
 hydrogen, and
- b) a mercapto ester comprising the reaction
 product of an optionally substituted
 mercaptohydrocarbylene-ol with a car-
 boxylic acid.

42. A composition according to Claim 41 in which
 the metal of the metal-containing heat stabilizer is
 calcium, barium, zinc, lead, tin or trivalent antimony
 and the mercapto ester has the formula



where R¹ and R², each independently, is optionally
 substituted hydrocarbylene and G is hydrogen, carboxy
 or $-\text{C}-\text{O}-\text{R}^3-\text{SH}$, where R³ is optionally substituted
 hydrocarbylene.

43. A composition according to Claim 42 in which R^1 and R^3 , each independently, is alkylene of 2 to 20 carbon atoms, R^2 is alkylene of 1 to 20 carbon atoms and R^1 , R^2 and R^3 each independently is alkenylene of 2 to 20 carbon atoms, cycloalkylene of 3 to 8 carbon atoms, arylene of 6 to 20 carbon atoms, alkarylene of 7 to 40 carbon atoms or aralkylene of 7 to 40 carbon atoms; R^1 , R^2 and R^3 being unsubstituted or substituted by one or more of hydroxyl, alkoxy of 1 to 20 carbon atoms, oxo, oxirane, alkoxycarbonyl of 2 to 20 carbon atoms, aryloxy carbonyl of 7 to 20 carbon atoms, acyl of 2 to 20 carbon atoms, acyloxy of 2 to 20 carbon atoms, chloro, bromo, iodo, fluoro, cyano, alkylamido of 2 to 20 carbon atoms, mercapto, alkylthio of 1 to 20 carbon atoms, alkylsulfamyl of 1 to 20 carbon atoms, alkylsulfonyl of 1 to 20 carbon atoms, alkyl of 1 to 20 carbon atoms, aryl of 6 to 20 carbon atoms, alkenyl of 2 to 20 carbon atoms and cycloalkyl of 3 to 8 carbon atoms, and where R^1 , R^2 and R^3 and their substituents are optionally substituted in the chain by one or more of oxygen, sulfur and nitrogen.

B 44. A composition according to Claim 43 in which G is hydrogen.

45. A composition according to Claim 44 in which R^2 is substituted or unsubstituted alkyl of 1 to 20 carbon atoms or alkenyl of 2 to 20 carbon atoms.

46. A composition according to Claim 45 in which R^2 contains 12 to 20 carbon atoms and R^1 is alkylene of 2 to 20 carbon atoms.

47. A composition according to Claim 46 in which R^1 is lower alkyl or hydroxyl lower alkyl and R^2 is stearyl, oleyl, linoleyl, myristyl or palmityl.

a 48. A composition according to Claim 47 in which the mercapto ester comprises 2-mercaptoethyl stearate/

or 2-mercaptoethyl oleate or 2-mercaptoethyl linoleate.

49. A composition according to Claim 41 in which the mercapto ester comprises an ester obtained by reacting a substituted or unsubstituted mercapto-loweralkanol with a carboxylic acid of 8 to 20 carbon atoms.

B 50. A composition according to Claim ⁴²~~43~~ in which R^2 is $\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{O}-\text{R}^3\text{SH} \end{array}$.

51. A composition according to Claim 50 in which R^2 is substituted or unsubstituted alkylene of 1 to 20 carbon atoms, alkenylene of 2 to 20 carbon atoms or arylene of 6 to 20 carbon atoms.

52. A composition according to Claim 51 in which R^1 and R^3 , each independently, is unsubstituted or substituted alkylene of 2 to 20 carbon atoms.

53. A composition according to Claim 52 in which R^2 is alkylene of 1 to 20 carbon atoms or alkenylene of 2 to 20 carbon atoms.

54. A composition according to Claim 53 in which R^1 and R^3 is lower alkylene or hydroxylower-alkylene.

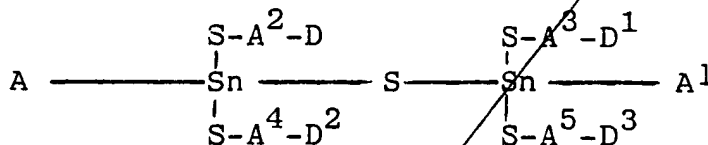
55. A composition according to Claim 43 in which the metal is calcium, barium, zinc, lead, tin or trivalent antimony.

Sub B⁵ 56. A composition according to Claim 43 in which the metal is tin.

57. A composition according to Claim 56 in which the tin-containing stabilizer comprises

dibutyltin maleate
dibutyltin di(stearyl maleate)
[monobutyltin(isooctylmercaptoacetate)-sulfide]
monobutyltin(dodecylmercaptide)sulfide
monobutyltin(mercaptoethyl oleate)sulfide
monobutyltin trimercaptoethyl oleate
monobutyltin(hydroxyethylmercaptide)(sulfide)

and bridged sulfur compounds of formula



where

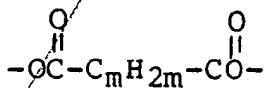
A and A¹ are lower alkyl;

A², A³, A⁴ and A⁵ are lower
alkylene;

D, D¹, D² and D³ each independently,

is

OH, - OC(=O) - (C₈-C₂₀ alkyl),
(C₆-C₁₈)alkyl, or where
D and D¹, or D² and D³ together form
the group



where m is a number from 0 to 8.

⁵⁸
~~59~~. A composition according to Claim ⁵⁷~~58~~ in which
the mercapto ester is a substituted or unsubstituted
mercaptoloweralkanol ester of a carboxylic acid of 8 to
20 carbon atoms.

ADD
f6

Add
H¹

Add
517

Add
L¹

Add
M⁴

Rule 126
B